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Polymer 40 (1999) 4505–4514

polymer

Direct synthesis of novel acidic and zwitterionic block copolymers via TEMPO-mediated living free-radical polymerization

L.I. Gabaston, S.A. Furlong, R.A. Jackson, S.P. Armes*

School of Chemistry, Physics and Environmental Science, University of Sussex, Falmer, Brighton BN1 9QJ, UK

Received 29 June 1998; received in revised form 24 September 1998; accepted 24 September 1998

Abstract

A series of novel acidic and zwitterionic water-soluble diblock copolymers has been synthesized directly (i.e. without protecting group chemistry) via the TEMPO-mediated living free-radical polymerization of various hydrophilic styrenic monomers. In all syntheses TEMPO-capped poly(sodium 4-styrenesulfonate) was utilized as a well-defined macro-initiator. Chain extension of this macro-initiator with 2-vinylpyridine proved very inefficient. Using 4-vinylbenzyltrimethylammonium chloride as comonomer led to an insoluble zwitterionic complex, whereas water-soluble zwitterionic block copolymers were obtained with 4-(dimethylamino)methylstyrene. Micellar solutions were obtained with the less hydrophilic 4-vinylbenzyl alcohol comonomer. A series of strong acid–weak acid block copolymers with varying sodium 4-styrene-sulfonate contents (20–80 mol%) were prepared via chain extension of the macro-initiator using sodium 4-styrenecarboxylate. These acidic block copolymers undergo reversible pH-induced aggregation in aqueous solution and ^{13}C n.m.r. spectroscopy studies suggest that the carboxylic acid block forms the hydrophobic micellar core. Dynamic light scattering studies indicate intensity-average micelle diameters of 20–60 nm.

Keywords: Block copolymers; TEMPO; Living free-radical polymerization

1. Introduction

In a series of recent papers [1–5] Georges' group at Xerox has described the use of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as a reversible capping agent to produce pseudo-living polymers via free-radical polymerization. This approach allows the synthesis of homopolymers of reasonably narrow molecular weight distribution ($M_w/M_n < 1.3$) and, perhaps more importantly, block copolymers via chain extension of TEMPO-capped macro-initiators. Furthermore, functional monomers such as sodium 4-styrenesulfonate can be homopolymerized directly in ethylene glycol–water mixtures to produce near-monodisperse poly(sodium 4-styrenesulfonate) in near-quantitative yield.

Various polystyrene-based blocks have been produced by this chain extension method. For example, poly(styrene-*b*-*p*-bromostyrene) blocks were synthesized by Yoshida [6] with polydispersities as low as 1.15 and molecular weights of ca. 20 000 g.mol^{-1}. A single example of a poly(chloromethylstyrene-*b*-styrene) copolymer of relatively high molecular weight (72 000 g.mol^{-1}) but rather high polydispersity ($M_w/M_n = 1.8$) was reported by Bertin and Boutevin [7]. Very recently, Lokaj et al. [8] obtained a range of styrene-2-(dimethylamino)ethyl methacrylate block copolymers with molecular weights as high as 70 000 g.mol^{-1} and polydispersities of around 1.25. A similar approach was recently reported by Bohrisch et al. [9] for the TEMPO-mediated synthesis of narrow polydispersity poly(4-vinylpyridines), which were subsequently converted to polycarboxybetaines and polysulfobetaines.

Recently we reported [10–14] the polymerization of a wide range of hydrophilic methacrylates and vinyl ethers via group transfer polymerization and living cationic polymerization, respectively, to produce new hydrophilic–hydrophilic water-soluble AB diblock copolymers. Such functional monomers often required protection prior to polymerization and subsequent deprotection was sometimes problematic. In particular, we have recently described [15] the synthesis of a series of novel zwitterionic 2-(dimethylamino)ethyl methacrylate–methacrylic acid block copolymers using 2-tetrahydropyranyl methacrylate as a protected monomer for the methacrylic acid residues. Deprotection via thermolysis was deemed unsuccessful since it led to a significant broadening in the molecular weight distribution of the zwitterionic copolymer compared with the precursor block. In contrast, deprotection via acidic hydrolysis under mild conditions was shown to be satisfactory. In related

* Corresponding author. Fax: + 44-1273-677196.
E-mail address: S.P.Armes@sussex.ac.uk (S.P. Armes)

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PII: S0032-3861(98)00689-2

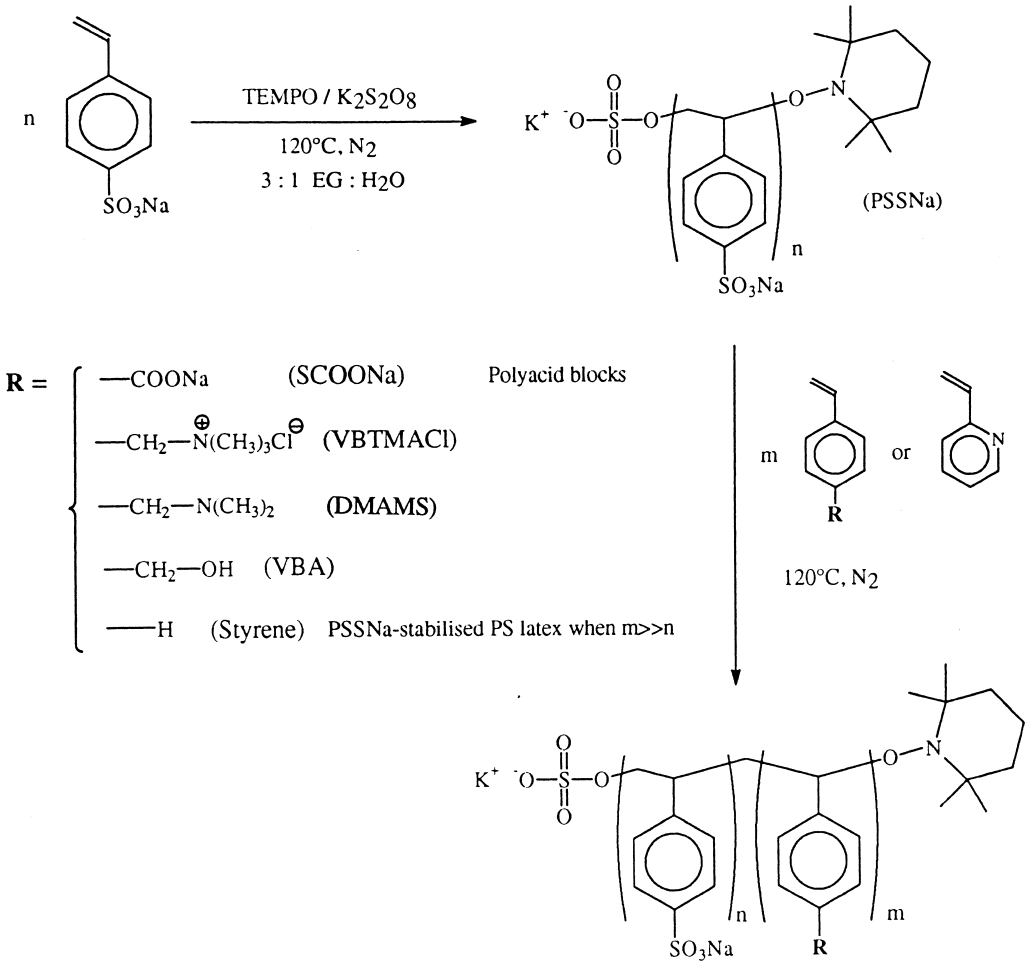


Fig. 1. Reaction scheme for the synthesis of water-soluble acidic and zwitterionic diblock copolymers via TEMPO-mediated living free-radical polymerization.

work, marked pH-induced surface activity was reported for hydrophilic–hydrophilic tertiary amine methacrylate block copolymers synthesized by group transfer polymerization. Subtle differences in hydrophilicity between 2-(dimethylamino)ethyl methacrylate (DMAEMA) and 2-(diethylamino)ethyl methacrylate (DEAEMA) residues were sufficient to cause DMAEMA–DEAEMA block copolymers to form micelles reversibly in aqueous solution.

In the present work we have used TEMPO-mediated living free radical polymerization to synthesize a series of novel zwitterionic and acidic water-soluble diblock copolymers directly, i.e. without using protecting group chemistry (see Fig. 1). These novel block copolymers exhibit interesting aqueous solution properties such as reversible pH-induced micellization.

2. Experimental

All reagents were purchased from Aldrich, except 4-vinylbenzyltrimethylammonium chloride (VBTMACl; Acros, UK) and 4-(dimethylamino)methylstyrene (DMAMS; Monomer–Polymer and Dajac Laboratories Inc., USA). Styrene was purified by passing through an alumina column to remove the hydroquinone monomethyl ether inhibitor.

The general procedure used to prepare the homopolymers was based on a procedure reported by the Xerox group [4,5]. The sodium 4-styrenesulfonate (SSNa) monomer (10 g), sodium bisulfite (0.17 g) and TEMPO (0.375 g) were added to a 3:1 w/w% ethylene glycol (EG)–water mixture (40 cm^3) and heated to 60°C under nitrogen. Potassium persulfate (0.33 g) was added at 60°C and this solution was stirred under nitrogen for 1 h. The reaction temperature was then raised to 120°C and the solution was stirred under nitrogen for a further 7–24 h. The resulting homopolymers were precipitated by pouring the reaction mixture into acetone (10-fold excess) and then isolated by filtration. In the case of VBTMACl, iso-propanol was used as a non-solvent for precipitation. Finally, the homopolymers were freeze-dried from water and then dried in a vacuum oven overnight.

The block copolymers were synthesized by the addition of the second monomer to a refluxing 3:1 ethylene glycol–water solution of TEMPO-capped poly(sodium 4-styrene-

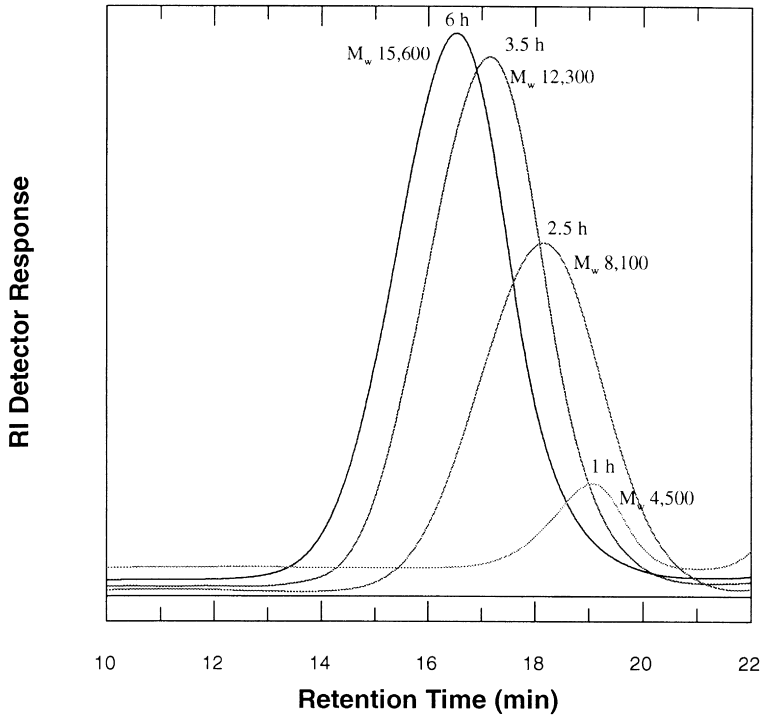


Fig. 2. GPC data for the synthesis of the poly(sodium 4-styrenesulfonate) macro-initiator. The peaks (1–6 h) shift to lower retention times (higher molecular weights) with increasing reaction time as expected.

sulfonate) macro-initiator (PSSNa) at 116°C under a nitrogen atmosphere for 24 h. The resulting block copolymer was precipitated by pouring the reaction solution into acetone (10-fold excess) and isolated by filtration. Reprecipitation from water into acetone was repeated until removal of the ethylene glycol was complete. The copolymers were finally obtained after freeze-drying from water and further drying in a vacuum oven overnight.

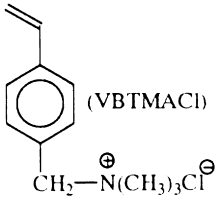
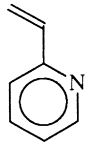
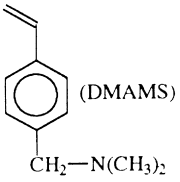
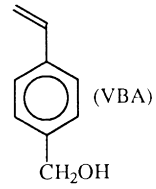
Molecular weights were determined by aqueous gel permeation chromatography (GPC) using a Superdex 200 HR 10/30 column (Pharmacia Biotech, Sweden) and a refractive index detector. Poly(sodium 4-styrenesulfonate) standards (Mp 1370–82 800 g.mol^{-1}) were used with a mobile phase of 20% acetonitrile/80% 0.05 M $NaNO_3$ + 0.01 M Na_2HPO_4 at a flow rate of 0.5 ml.min^{-1}. FTi.r. spectra were recorded from either KBr discs or using a 'Golden Gate' diamond ATR accessory (Specac, UK) using a Nicolet Magna 550 Series II spectrometer at 4 cm^{-1} resolution. ^{1}H n.m.r. spectra of (co)polymer solutions in D_2O or D_2O/DCl were recorded using a Bruker Avance 300 MHz spectrometer and ^{13}C n.m.r. spectra (125 MHz) were recorded with a Bruker AMX 500 MHz spectrometer. In both cases, 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid, sodium salt was used as the internal standard. Elemental microanalyses were performed by Medac Ltd (Brunel University). Dynamic light scattering measurements were made on 1 w/v% aqueous solutions using a Malvern instrument with a 75 mW argon ion laser at a detection angle of 90°.

3. Results and discussion

3.1. Poly(sodium 4-styrenesulfonate) macro-initiator

SSNa was polymerized in a 3:1 ethylene glycol–water mixture at 120°C using potassium persulfate initiator in the presence of TEMPO (TEMPO/initiator molar ratio = 2) as described by the Xerox group [4,5]. The resulting TEMPO-capped poly(sodium 4-styrenesulfonate) (PSSNa) was isolated in high yield (ca. 90%) by precipitation into acetone and subsequently characterized by aqueous GPC using near-monodisperse poly(sodium 4-styrenesulfonate) calibration standards. This indicated an M_n of ca. 13 000 and an M_w/M_n of 1.22. In a second experiment an M_n of ca. 11 000 and an M_w/M_n of 1.21 was obtained. A kinetic study of the polymerization of SSNa was achieved by periodic extraction of aliquots from the reaction solution. Representative gel permeation chromatograms are shown in Fig. 2. The extent of conversion, and hence molecular weight, increased linearly for the first 5 h, and polydispersities decreased with increasing reaction time. These results are similar to those reported by the Xerox group. This PSSNa homopolymer was then used as a macro-initiator in chain extension reactions at 112–119°C with several hydrophilic styrenic comonomers (see Fig. 1), including 4-styrenecarboxylic acid, VBTMACl, 2-vinylpyridine (2VP), DMAMS, 4-vinylbenzyl alcohol (VBA) and styrene (see Table 1).

Table 1
A summary of the block compositions, calculated molecular weights, yields and solubilities of various block copolymers synthesized by TEMPO-mediated living free-radical polymerization

Chemical structure of comonomer	Expected block copolymer composition (mol% SSNa)	Actual block composition microanalysis[a] (mol% SSNa)	M_n of block copolymer[b]	Overall yield (%)	Solubility
 (VBTMACl)	51 37	51 49	21 800 22 800	40 22	insoluble in all solvents
 (2VP)	34	92	11 500	32	water soluble
 (DMAMS)	44	60	16 700	58	water soluble
 (VBA)	39	63	18 000	61	water soluble

[a] Calculated from the S/N ratio or reduced S %, as appropriate.
[b] Calculated from the M_n of the PSSNa macro-initiator and the block copolymer composition, as determined by microanalyses. M_n of macro-initiator was 11 000, except in the case of VBA where it was 13 000.

3.2. Zwitterionic block copolymers

Block copolymerization of PSSNa with 2VP at 120°C gave a sulfonate-rich block (92 mol% by elemental analyses, compared with the expected 34 mol% composition), indicating a very slow rate of polymerization of 2VP under these conditions. This is consistent with a recent paper by Jaeger and co-workers [4], who reported that the rate of TEMPO-mediated polymerization of 4-vinylpyridine in bulk at 130°C was only 0.85% per hour. Thus, only very slow block copolymerization of 2VP would be expected in solution at 120°C.

In contrast, block copolymerization using the VBTMACl monomer led to the precipitation of a zwitterionic complex which proved to be insoluble in a wide range of solvents (THF, DMF, NMP, 2,2,2-trifluoroethanol, water, aqueous NaCl, HCl, NaOH, dimethylsulfoxide and acetonitrile). Microanalytical data confirmed that the sulfur/nitrogen molar ratio of this complex was approximately 1.0, so presumably it was the target 50:50 zwitterionic block copolymer (see entry 1 in Table 1). The synthesis of an asymmetric 37:63 (VBTMACl-rich) block copolymer was also attempted, but again a 50:50 block was obtained as an insoluble complex (see entry 2 in Table 1). In this context, it is noteworthy that the homopolymerization of VBTMACl proceeded to high yield. Furthermore, Varoqui et al. [16] reported that poly(2-vinylpyridine-b-sodium 4-styrenesulfonate) zwitterionic blocks exhibited similarly limited solubility in aqueous media. However, Michaels and Miekka [17] studied the aqueous solution behaviour of mixtures of

Table 2
A summary of the block copolymer compositions and calculated molecular weights of acidic SSNa–SCOONa block copolymers synthesized using TEMPO-mediated living free-radical polymerization

Expected block copolymer composition mol% SSna	M_n[a] of PSSNa macro-initiator	Actual block copolymer composition (mol% SSNAa)		Calculated overall M_n of block[d] ($g\,mol^{-1}$)
		n.m.r.[b]	S %[c]	
100	11 000	100	100	11 000
83	11 000	87	95	12 400
76	13 000	80	72	15 700
54	13 000	56	51	21 400
45	13 000	45	44	26 100
25	13 000	22	21	51 000
17	13 000	21	16	53 300

[a] Obtained from aqueous GPC (Superdex column, 0.5 $ml.min^{-1}$, RI detector, eluent: 20% acetonitrile 80% 0.05 M $NaNO_3$ + 0.01 M Na_2HPO_4, PSSNa standards).
[b] Calculated from ^{13}C n.m.r. spectroscopy in D_2O (see text for further details).
[c] Calculated using the reduced sulfur contents of the block copolymers compared with the PSSNa homopolymer as determined from elemental microanalyses.
[d] Calculated from a combination of the macroinitiator M_n and the block copolymer composition as determined by ^{13}C n.m.r. spectroscopy.

PVBTMACl and PSSNa homopolymers and also obtained insoluble 1:1 complexes. Thus precipitation does not in itself constitute proof of successful block copolymerization: it is conceivable that thermal (i.e. non-living) homopolymerization of VBTMACl in the presence of the SSNa homopolymer could also lead to the formation of an insoluble complex.

The PSSNa macro-initiator was also reacted with DMAMS and, in this case, a soluble block copolymer containing 40 mol% DMAMS, as calculated from nitrogen and sulfur microanalyses, was successfully synthesized (N.B. the expected composition was 56 mol% DMAMS, indicating incomplete polymerization of the second monomer). This 60:40 PSSNa–PDMAMS block copolymer was dissolved in DCl/D_2O and characterized by ^1H n.m.r. spectroscopy. Two additional peaks were found in the block copolymer spectrum compared with that for the PSSNa homopolymer. These signals correspond to the dimethylamino protons (δ 2.37), and the methylene protons (δ 3.89) of the DMAMS residues. Comparing the integrals of these signals to the integral for the aromatic signals (δ 5.7–7.7) enabled an SSNa content of 57 mol% to be estimated, which is in good agreement with the block composition determined from elemental analyses. This block copolymer was soluble in water. However, on addition of HCl, protonation of the amine residues occurred, leading to macroscopic precipitation of the zwitterionic block copolymer at its isoelectric point. Redissolution occurred on addition of base. Similar aqueous solution behaviour has been reported for other zwitterionic block copolymers by Lowe et al. [10,15].

Finally, the PSSNa macro-initiator was reacted with VBA. Sulfur microanalyses indicate a VBA content of 37 mol% for the resulting block copolymer. This block copolymer remained soluble in the 3:1 ethylene glycol–water reaction mixture but bluish solutions (due to Tyndall scattering) were obtained on redissolution in water. Photon correlation spectroscopy studies of these aqueous solutions at pH 6 revealed the presence of micelles, with an intensity-average diameter of approximately 70 nm. In addition, ^1H n.m.r. studies in D_2O showed no evidence of the benzyl alcohol group, which indicates that the relatively hydrophobic VBA block forms the non-solvated micellar core.

Very recently Mülhaupt and co-workers [18] reported using TEMPO-mediated free radical chemistry for the attempted dispersion polymerization of styrene in *n*-decane at 135°C with a 'Kraton' block copolymer stabilizer. The use of homopolymer steric stabilizers such as poly(*N*-vinylpyrrolidone) for polystyrene latex syntheses via TEMPO-mediated dispersion polymerization in non-aqueous media has also been independently investigated in our group [19]. In the present study, poly(sodium 4-styrenesulfonate) was employed as a macro-initiator/steric stabilizer for styrene monomer in a 3:1 ethylene glycol–water mixture. As expected, this led to the formation of colloidally stable polystyrene latex particles stabilized by terminally grafted PSSNa chains. Due to the relatively low reaction temperature (*ca.* 110°C) only a relatively poor yield of latex (< 10%) was obtained. Scanning electron microscopy studies confirmed that the latex particles had a spherical morphology but also a very polydisperse particle size distribution (particle diameters ranged from 0.3 to 30 μm). Sulfur microanalyses of the dried latex particles indicated a PSSNa content of 6.7 wt%. An FTi.r. spectrum of the latex was very similar to that of polystyrene homopolymer, with several additional weak bands due to the PSSNa steric stabilizer visible at 1008, 1039, 1126 and 1174 cm^{-1}.

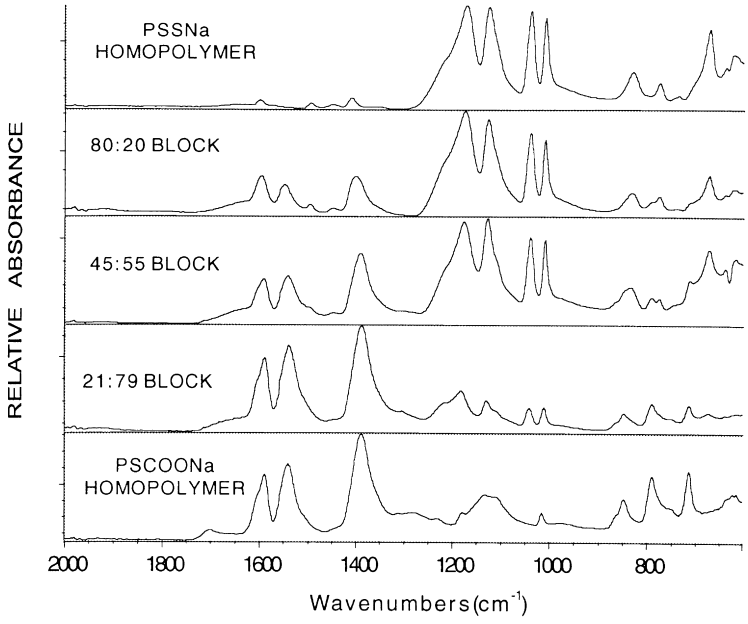


Fig. 3. FTi.r. spectra of PSSNa homopolymer, PSCOONa homopolymer and PSSNa–PSCOONa block copolymers of various compositions (21–80 mol%).

3.3. Acidic block copolymers

Chain extension of the PSSNa macro-initiator did not occur with 4-styrenecarboxylic acid which was synthesized from 4-carboxybenzyltriphenylphosphonium bromide in 95% yield using Wittig chemistry according to a literature procedure [20]. This observation is perhaps surprising, since Georges and co-workers have shown that acidic additives such as camphorsulfonic acid can enhance the rate of TEMPO-mediated polymerizations [21]. However, reasonable block copolymer yields (up to 83%) were obtained using the sodium salt of this monomer (SCOONa). Varying the molar ratio of SCOONa relative to the PSSNa macro-initiator led to the formation of a series of water-soluble acidic block copolymers of varying compositions (ranging from 18 to 87 mol% SSNa, see Table 2). There were three reasons for choosing PSSNa as the macro-initiator rather than PSCOONa. Firstly, SSNa homopolymerization proceeded more efficiently and to higher yield. Secondly, PSSNa calibration standards were available, thus no systematic errors were incurred in obtaining molecular weight data by aqueous GPC. Finally, the PSSNa block remained hydrophilic and water-soluble at low pH, thus any homopolymer contamination resulting from incomplete initiation with SCOONa would be unlikely to affect the micelle studies (see later).

Using PSSNa and PSCOONa homopolymers as reference materials to aid spectral assignments, FTi.r. spectroscopy studies confirmed the presence of both the sulfonate and carboxylate residues in the acidic block copolymers (see Fig. 3). Furthermore, the relative intensities of several bands at 1593, 1545 (C=O asymmetric stretch) and 1394 cm^{-1} (C=O symmetric stretch) corresponding to the SCOONa residues, increased in accordance with the block compositions determined from sulfur microanalyses. More accurate block copolymer compositions were obtained using ^{13}C n.m.r. spectroscopy (^{1}H n.m.r. spectroscopy studies were also attempted but this technique proved incapable of distinguishing between the two comonomer residues). Again, using PSSNa and PSCOONa homopolymers to aid spectral assignments, ^{13}C resonances at 136 and 143 ppm were identified as being due to the aromatic **C**-COONa and **C**-SO_3Na carbon atoms in the SCOONa and SSNa residues, respectively; these peak integrals were then compared to obtain block compositions (using appropriate delay times to ensure reliable quantitative integration). Reasonably good agreement between these block compositions and those determined by sulfur microanalyses were obtained (see Table 2).

Problems were encountered in characterizing the acidic block copolymers by aqueous GPC. The SSNa and SCOONa homopolymers required rather different eluent conditions in order to avoid column adsorption problems. Thus we were unable to establish a suitable protocol for the GPC analysis of the SSNa–SCOONa copolymers in order to confirm chain extension and block copolymer formation. However, since PSSNa calibration standards were utilized, the molecular weight of the PSSNa macro-initiator could be accurately determined from aqueous GPC. In addition, the block compositions were known from the ^{13}C n.m.r. analyses and the sulfur contents. Thus, assuming that block copolymer formation was 100% efficient, the overall block copolymer molecular weights could be calculated. A similar approach was adopted by Lokaj et al. [8] for the characterization of PS–PDMAEMA block copolymers.

It is, of course, possible that, during the attempted block

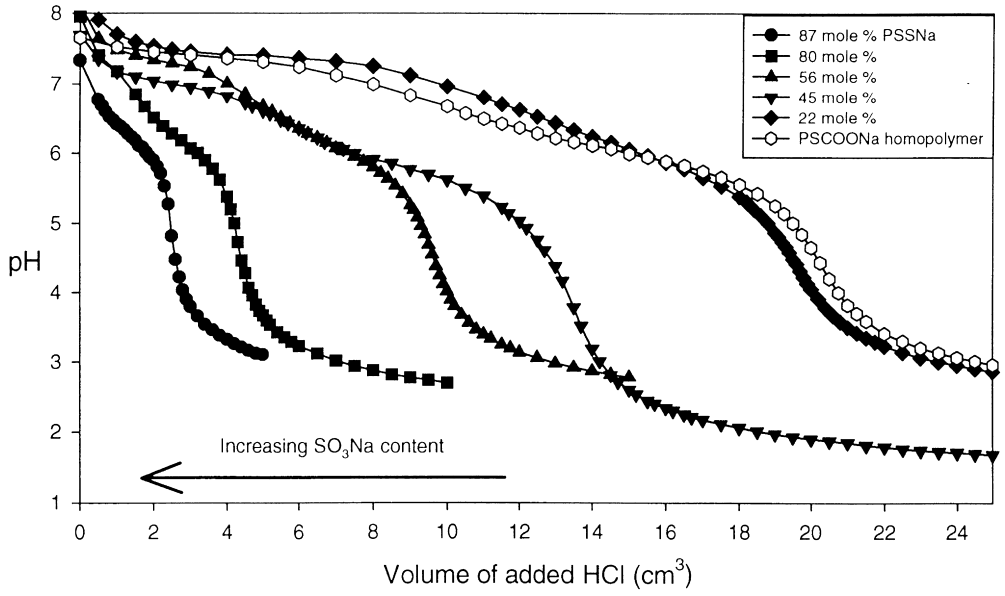
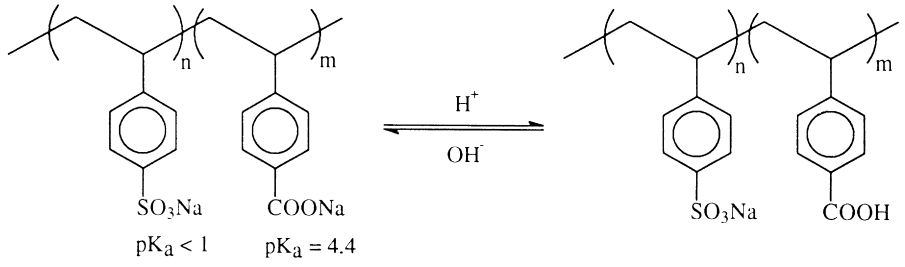


Fig. 4. Acid titration curves for the PSCOONa homopolymer and selected PSSNa–PSCOONa block copolymers.

copolymer syntheses, the second monomer (SCOONa or 2-VP, DMAMS, VBTMACl, VBA) merely thermally polymerized via non-living free-radical chemistry to give a polydisperse homopolymer, without the desired chain extension of the PSSNa macro-initiator. However, good evidence for genuine block copolymer formation was obtained from our studies of the aqueous solution properties of the acidic block copolymers. Aqueous solutions of the acidic blocks and the SCOONa homopolymer, initially at neutral pH, were titrated with dilute HCl (see Fig. 4). On protonation, the SCOONa homopolymer (and SCOONa-rich block copolymers) became hydrophobic and precipitated from solution. However, acidic block copolymers containing 21–56 mol% SSNa formed stable micellar



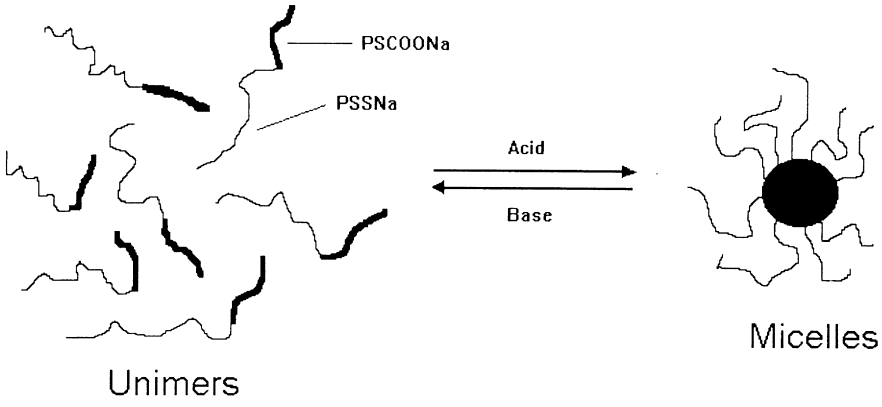


Fig. 5. Schematic representation of pH-induced micelle formation by the PSSNa–PSCOONa acidic block copolymers.

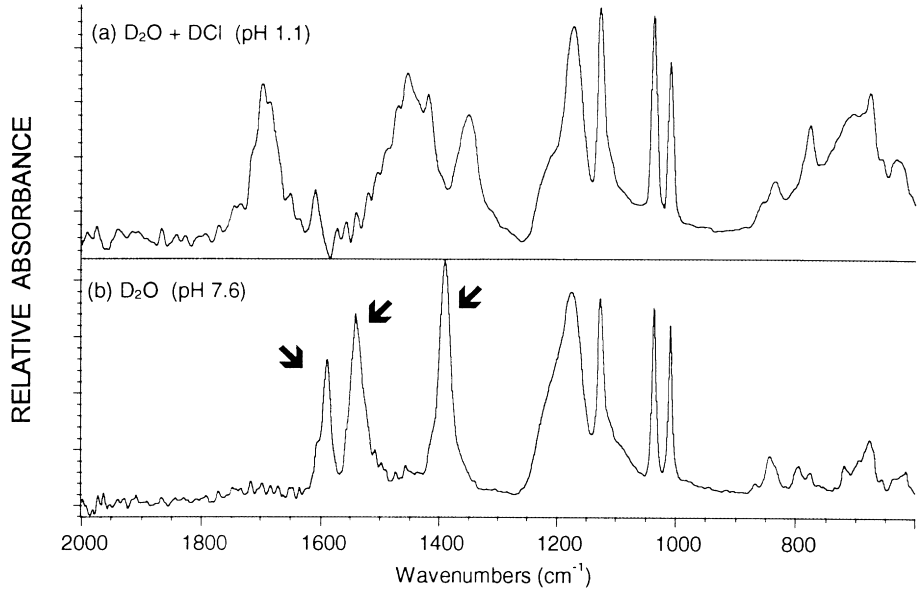


Fig. 6. FTi.r. spectra in D_2O of a 56:44 PSSNa–PSCOONa block copolymer at (a) pH 1.1; and (b) pH 7.6.

solutions (see Fig. 5), with no visible precipitation. Such micellization behaviour is well known for block copolymers and is extremely unlikely for physical mixtures of the SSNa and SCOONa homopolymers (since these are both anionic polyelectrolytes the net electrostatic interactions are repulsive, in contrast to the net attractive interaction found for the zwitterionic blocks). FTi.r. spectra of concentrated solutions (*ca*. 10 w/v% in D_2O) of a 56:44 acidic block copolymer were recorded using a diamond ATR accessory. At pH 7.6 all the SCOONa residues were present in their ionized form. Three absorption bands corresponding to the anionic carboxylate groups were observed at 1590, 1541 and 1391 cm^{-1}. However, at pH 1.1 these three bands disappeared and were replaced by several new bands characteristic of the neutral carboxylic acid moieties (at 1698 (ν C=O), 1457 (δ O–H) and 1350 (δ C–O) cm^{-1}), see Fig. 6. Dynamic light scattering studies were also carried out on selected acidic block copolymers. For example, it was confirmed that a 56:44 block copolymer molecularly dissolved in water at pH 7. Adjusting the solution pH with

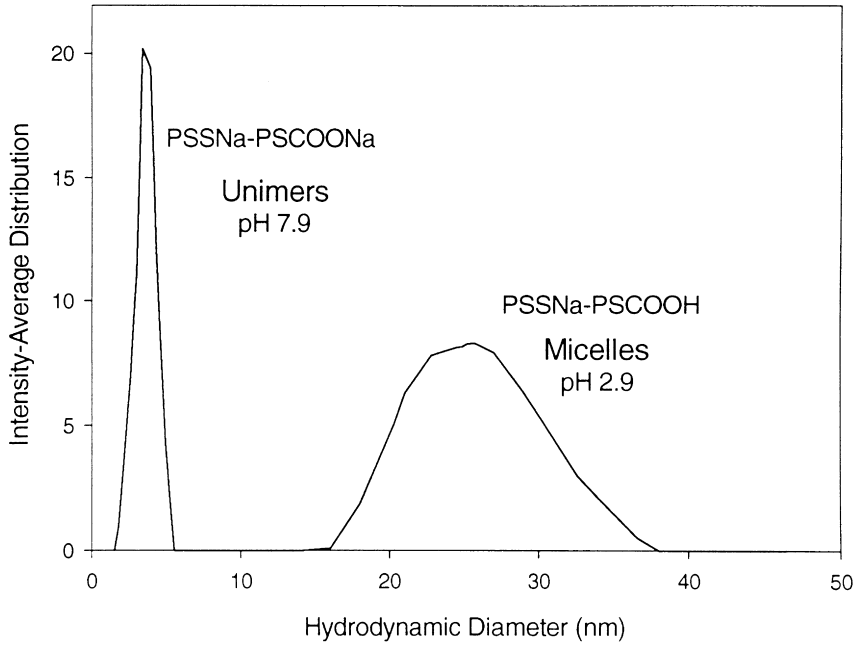


Fig. 7. Hydrodynamic size of a 56:44 block copolymer (dissolved in water as a 1.0% w/v solution at 25°C and then titrated to pH 2.9 using HCl) as determined by photon correlation spectroscopy.

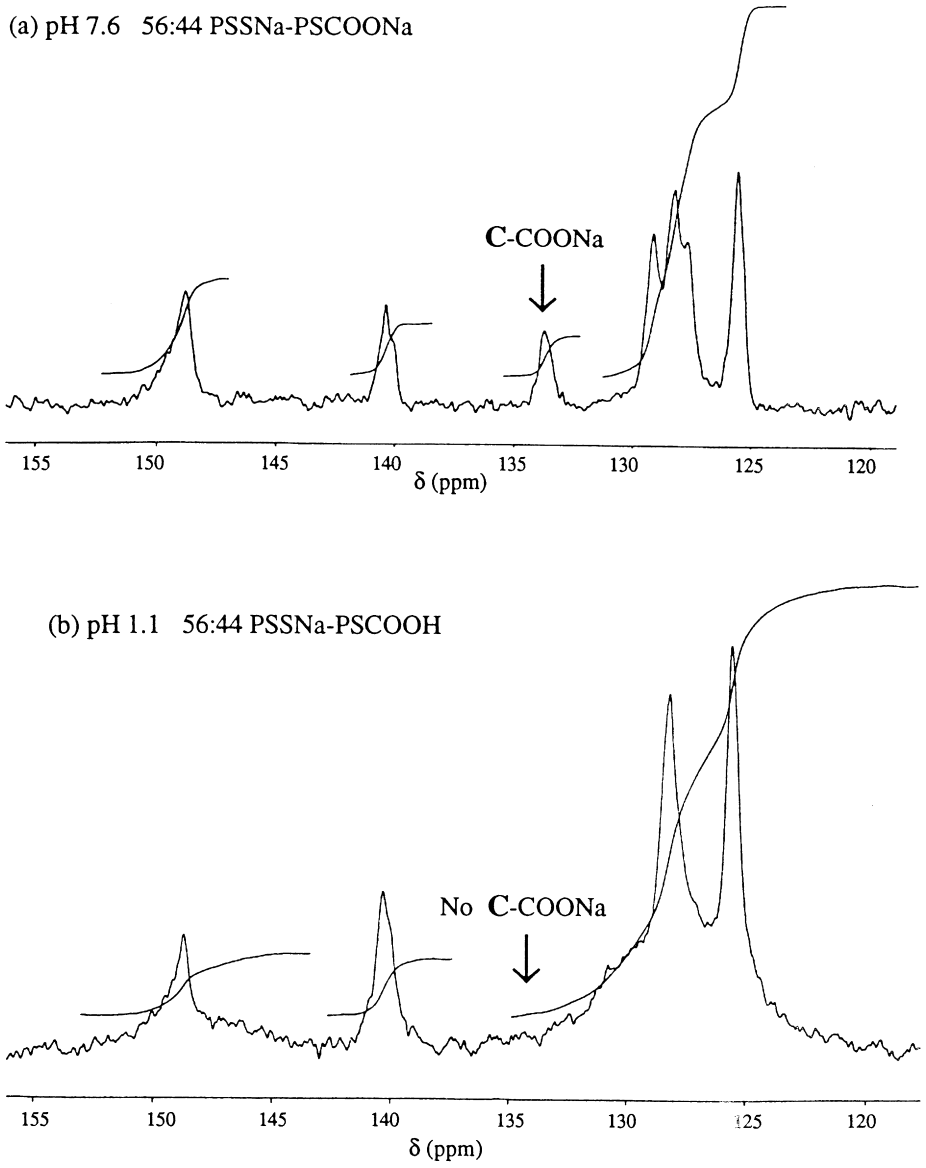


Fig. 8. ^{13}C n.m.r. spectra for a 56:44 PSSNa–PSCOONa block copolymer in (a) D_2O at pH 7.6; and (b) D_2O/DCl at pH 1.1. Note the disappearance of the ^{13}C n.m.r. signals (e.g. at 134 ppm) due to the PSCOONa in the acidic medium, indicating that this block forms the non-solvated micellar core.

HCl led to selective protonation of the weakly acidic carboxylate groups, with the more acidic sulfonate groups remaining ionized. As the anionic charge is removed from the carboxylate acid block it becomes hydrophobic, causing micellization of the acidic block copolymer and hence a marked increase in the intensity of the scattered light. Dynamic light scattering measurements indicated an intensity-average micelle diameter of ca. 20 nm at pH 3.9. This micellization is completely reversible: on addition of base the carboxylic acid groups ionize and the micellar aggregates dissociate into unimers. Our initial results suggest that the PSSNa content of the block copolymers has a pronounced effect on micellization behaviour. Thus, acidic copolymers with SSNa contents of 80 mol% or higher do not undergo micellization in acidic solution. Copolymers containing 45 to 56 mol% SSNa residues form stable micelles of ca. 20–25 nm diameter (see Fig. 7), whereas rather larger micelles of 65 nm, and also micellar aggregates, are formed by copolymers containing 20–21 mol% SSNa residues. It is noteworthy that the micellization behaviour of these acidic block copolymers is complementary to that of the tertiary amine methacrylate block copolymers reported by Bütün and co-workers [11]. The latter blocks are molecularly dissolved in acidic solution and form micelles at around pH 7–8.

^{13}C n.m.r. spectroscopy studies of concentrated aqueous solutions of the block copolymers at different solution pH are also consistent with the acid titration and dynamic light scattering data. At pH 7.6 all the resonances corresponding to the PSSNa and the PSCOONa blocks were present,

whereas at pH 1.1 only the resonances corresponding to the sulfonate residues of the block were observed (see Fig. 8). The disappearance of the n.m.r. signals assigned to the SCOONa residues (e.g. that due to the C-COONa carbon normally found at ca. 134 ppm) indicates poor solvation and/or reduced mobility for this block. Thus these ^{13}C n.m.r. studies provide strong supporting evidence for the PSCOONa block forming a relatively hydrophobic (low water content) micelle core and the PSSNa block forming the solvated micellar corona, as expected. This micelle structure is consistent with the effect of block composition on micelle formation noted above.

4. Conclusions

In summary, several novel zwitterionic and strong acid–weak acid block copolymers have been synthesized directly (i.e. without using protecting group chemistry) via TEMPO-mediated living free-radical chemistry in aqueous ethylene glycol mixtures using PSSNa as a macro-initiator. Only inefficient block copolymerization was achieved with the 2VP comonomer. An insoluble complex was formed with VBTMACl. The most interesting class of zwitterionic blocks appear to be those based on PSSNa–PDMAMS: further studies of the aqueous solution properties of these latter copolymers are currently in progress.

Depending on their block composition, PSSNa-PSCOONa acidic copolymers can undergo reversible pH-induced micellization in aqueous solution on addition of acid. In the absence of GPC data, micellar aggregation is the best available evidence for genuine block copolymer formation. Since it is more easily protonated, the more weakly acidic PSCOONa block forms the hydrophobic micellar core, while the PSSNa chains remain anionic, forming the solvated corona. Intensity-average micelle diameters are in the 20–60 nm range. The micellization behaviour of the acidic copolymers is complementary to the tertiary amine methacrylate blocks reported earlier, since the latter copolymers aggregate at around neutral pH on addition of base.

Acknowledgements

We thank the EPSRC (GR/K49232) for a post-doctoral fellowship for L.I. Gabaston. An EPSRC ROPA grant (GR/K86855) was used to purchase the argon ion laser for the dynamic light scattering studies.

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